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ENGINEERING CHANGE NOTICE

Page 1 of 2

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Tank Characterization Report for Single-Shell Tank 241-B-201

John M. Conner

Lockheed Martin Hanford, Corp., Richland, WA 99352 U.S. Department of Energy Contract DE-AC06-96RL13200

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Abstract: This document summarizes the information on the historical uses, present status; and the sampling and analysis results of waste stored in Tank 241-B-201. This report supports the requirements of the Tri-Party Agreement Milestone M-44-05.

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3.0 BEST-BASIS INVENTORY ESTIMATE

Information about the chemical and/or physical properties of tank wastes is used to perform safety analyses, engineering evaluations, and risk assessments associated with waste management activities, as well as to address regulatory issues. Waste management activities include overseeing tank farm operations and identifying, monitoring, and resolving safety issues associated with these operations and with the tank wastes. Disposal activities involve designing equipment, processes, and facilities for retrieving wastes and processing the wastes into a form that is suitable for long-term storage.

Chemical inventory information generally is derived using two approaches: 1) component inventories are estimated using the results of sample analyses; and 2) component inventories are predicted using a model based on process knowledge and historical information. The most recent model was developed by Los Alamos National Laboratory (LANL) (Agnew et al. 1997). Not surprisingly, information derived from these two different approaches is often inconsistent.

An effort is underway to provide waste inventory estimates that will serve as standard characterization information for the various waste management activities (Hodgson and LeClair 1996). Appendix D contains the complete narrative regarding the derivation of the inventory estimates presented in Tables 3-1 and 3-2.

Table 3-1. Sampling-Based Best-Basis Inventory Estimates for Nonradioactive Components in Tank 241-B-201 (October 18, 1996).

Analyte	Total Inventory (kg)	Basis (S, M, or E) ²	Comment
Al	473	S	
Bi	13,000	S	
Ca	1,680	S	
Cl	227	S	
CO ₃	0	М	
Cr	459	S	
F	802³	S	Water soluble only
Fe	1,840	S	,
Hg	0.0824	S	
K	799	S	
La	2,080	S	
Mn	2,640	S	
Na	5,250	S	

Ni	65.9	S	
NO ₂	121	S	
NO ₃	6,780	S	
OH⁴	8,520	С	Charge balance calculation
Pb	187	S	
P as PO ₄	2,300	S	
Si	2,780	S	
S as SO ₄	47.9	S	
Sr	127	S	
TOC	325	S	
\mathbf{U}_{total}	21.5	S	
Zr	1.47	S	

Notes:

Table 3-2. Best-Basis Inventory Estimate for Radioactive Components in Tank 241-B-201, Decayed to January 1, 1994 (Effective July 2, 1996). (2 Sheets)

Analyte	Total Inventory (Ci)	Basis (S,M, or E) ¹	Comment
^{3}H	5.63 E-04	M	
¹⁴ C	0.0435	S	
⁵⁹ Ni	4.96 E-05	M	
⁶⁰ Co	5.60 E-05	M	
⁶³ Ni	0.00457	M	
⁷⁹ Se	3.68 E-05	M	
⁹⁰ Sr	287	S	
⁹⁰ Y	287	S	Based on 90Sr
^{93m} Nb	1.45 E-04	M	
⁹³ Zr	1.75 E-04	M	
⁹⁹ Tc	0.267	S	
¹⁰⁶ Ru	4.20 E-11	M	
^{113m} Cd	4.89 E-04	M	
¹²⁵ Sb	6.46 E-05	M	

¹See Table B3-12.

²S = Sample-based, M = Hanford Defined Waste model, E = Engineering assessment-based ³Fluoride is based on water soluble portion only.

 $^{^4}$ C = Calculated by charge balance; includes oxides as hydroxides, not including CO₃, NO₂, NO₃, PO₄, SO₄, and SiO₃.

Table 3-2. Best-Basis Inventory Estimate for Radioactive Components in Tank 241-B-201, Decayed to January 1, 1994 (Effective July 2, 1996). (2 Sheets)

Analyte	Total	Basis	Comment
Amaryte	Inventory	(S,M, or E) ¹	Comment
	(Ci)	(-,,	
¹²⁶ Sn	5.55 E-05	M	
¹²⁹ I	2.29 E-06	M	·
¹³⁴ Cs	2.78 E-06	M	
^{137m} Ba	104	S	Based on ¹³⁷ Cs
¹³⁷ Cs	110	S	·
¹⁵¹ Sm	0.139	M	
¹⁵² Eu	1.82 E-04	M	
¹⁵⁴ Eu	0.602	S	
¹⁵⁵ Eu	0.0164	M	
²²⁶ Ra	8.22 E-09	M	
²²⁷ Ac	4.34 E-08	M	
²²⁸ Ra	5.29 E-13	M	
²²⁹ Th	1.02 E-10	M	:
²³¹ Pa	1.00 E-07	M	
²³² Th	4.62 E-14	M	
²³² U	5.36 E-08	M	
²³³ U	2.45 E-09	M	
²³⁴ U	0.00267	M	
²³⁵ U	1.19 E-04	M	
²³⁶ U	2.33 E-05	M	
²³⁷ Np	7.51 E-06	M	
²³⁸ Pu	3.21 E-04	M	
²³⁸ U	0.00271	M	
^{239/240} Pu	155	S	
²⁴¹ Am	4.26	S	
²⁴¹ Pu	0.0135	M	
²⁴² Cm	3.70 E-06	M	
²⁴² Pu	6.23 E-08	M	
²⁴³ Am	3.08 E-09	M	
²⁴³ Cm	7.98 E-08	M	
²⁴⁴ Cm	7.84 E-08	M	

Table 3-2. Best-Basis Inventory Estimate for Radioactive Components in Tank 241-B-201. Decayed to January 1, 1994 (Effective July 2, 1996). (2 Sheets)

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¹S=Sample-based

M=Hanford Defined Waste model-based

E=Engineering assessment-based

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APPENDIX D

EVALUATION TO ESTABLISH BEST-BASIS INVENTORY FOR TANK 241-B-201

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APPENDIX D

EVALUATION TO ESTABLISH BEST-BASIS INVENTORY FOR TANK 241-B-201

D1.0 INVENTORY EVALUATION

The following evaluation provides an engineering assessment of tank 241-B-201 contents. For this evaluation, the following assumptions are made:

- Tank waste mass is calculated using the measured density and the tank volume listed in Hanlon (1996). Both analytical-based and model-based inventories are derived using this volume. As a result, inventory comparisons are made on the same volume basis.
- Only the 224 waste stream contributed to solids formation. It is assumed that tanks with the same waste type will have the same concentrations of individual analytes.
- Bulk component (chemical specie) information is sufficient for comparing analytical and computed data sets. This information can be obtained from technical flowsheets (see Table D1-1).
- No radiolysis of NO₃ to NO₂ and no additions of NO₂ to the waste for corrosion purposes are factored into this evaluation.
- All Bi and Mn precipitate.
- No Si from blowsand is factored into this evaluation.
- All NO₃, C₂O₄, K, and Na remain dissolved in the interstitial liquid.
- Only the 224 waste stream contributes to the interstitial liquid.
- Concentration of components in interstitial liquid is based on a void fraction of 0.834 as reported by Agnew et al. (1996).
- La, Cr, PO₄, SO₄, and F partition between the liquid and solid phases.

Technical flowsheet information (Schneider 1951, and Kupfer et al. 1997) for 224 streams is shown in Table D1-1. The chemical species are reported without charge designation per the best-basis inventory convention. The comparative LANL-defined waste streams are also shown

in this table. The complete LANL inventory is shown in Table A3-1 of Appendix A. The sampling inventory is shown in Table B3-12 of Appendix B.

Table D1-1. Technical Flowsheet and HDW Defined Waste Streams.

Analyte	Flowsheet 224 ^t (M)	Flowsheet 224 ² (M)	HDW 224' (M)
Bi	0.00595	0.00565	0.006
C_2O_4	0.0459	0.0147	0.03
Cr	0.00362	0.00327	0.004
F	0.272	0.295	0.31
K	0.223	0.218	0.271
La	0.00376	0.00353	0.015
Mn	0.00514	0.00601	0.005
Na	1.62	1.60	1.8
NO ₃	1.06	0.684	1.582
PO ₄	0.0322	0.0321	0.049
SO ₄	0.00140	0.00364	0.002
NH ₄	nr	0.0067	nr

Notes:

D1.1 BASIS FOR CALCULATIONS USED IN THIS ENGINEERING EVALUATION

Because analytical data from a recent sampling event exists for tank 241-B-201, a throughput or concentration factor was derived. For those analytes that partially precipitated, a partitioning factor was also calculated.

One method of evaluating this tank would be to use fuel reprocessing records, flowsheet values, and waste transfer records; however, not all of these records are available for tank 241-B-201. With the concentration factor and the HDW reported void fraction or porosity (0.834), the inventory of soluble and insoluble analytes listed in the 224 facility waste stream flowsheets can be calculated.

¹Schneider (1951)

²Appendix C of Kupfer et al. (1997)

³Agnew et al. (1996)

D1.2 THROUGHPUT OR CONCENTRATION FACTOR

The concentration factor (CF) is derived using a flowsheet component that is assumed to be 100 percent insoluble. In this case, bismuth was used. The CF was determined by dividing the bismuth inventory found in the sample analysis by the bismuth inventory in the original waste stream (from the flowsheet). It is assumed that bismuth is 100 percent precipitated and that for each waste discharge pass through the tank, all of the bismuth was retained in the tank. The bismuth-based CF factor for tank 241-B-201 is calculated as follows:

CF =
$$13,000 \text{ kg}_{Bi} \div (0.00595 \text{ moles}_{Bi}/L_{224} \text{ x } 29 \text{ kgal}_{224} \text{ x } 3785 \text{ L/kgal x } 208.98 \text{ g/mole}_{Bi} \text{ x kg/1000 g)}$$

$$CF = 95$$

This same factor is used to calculate inventories for all analytes that precipitate in the tank. If the factor is valid and the flowsheet and the analytical data are correct, then inventories predicted by this investigation should be close to those reported in the analytical data. Tanks of the same waste type should have the same CF.

D1.3 PARTITIONING FACTOR

Once CFs for fully precipitated components for a waste type are determined, the sample analysis can be used to establish the way in which other components such as SO₄ or PO₄ partition between solids and supernate. For example, if the CF for bismuth is determined to be 95 for 224 waste, and the CF for PO₄ is 6.8, it can be concluded that 7 percent of the PO₄ in the neutralized process waste partitions to the waste solids, that is, the partitioning factor is 0.07.

Using this method, the estimated partitioning factor for other components for 224 waste based on tank 241-B-201 are as follows when using a CF of 95 for fully precipitated components:

 SO_4 : 0.03 La: 0.38 Cr: 0.23 PO_4 : 0.07 F: 0.015

D1.4 SAMPLE CALCULATIONS USED IN THIS ENGINEERING EVALUATION

Note: Both Schneider (1951) and Place (Kupfer et al. 1997) flowsheets were used; calculations are shown only for the Schneider flowsheet. In most cases, these values are similar; when they are different, the different results are discussed.

Components assumed to precipitate (Mn)

Mn:

0.00514 moles_{Bi}/L₂₂₄ x 29 kgal₂₂₄ x 3785 L/kgal x 54.94 g/mole_{Bi} x 95

CF x MT/1e6 g = 2.94 MT

Components assumed to remain dissolved in the interstitial liquid (NO₃, K, Na)

NO₃:

 $1.06 \; moles_{NO3}/L_{224} \; x \; 0.834_{porosity} \; x \; 3785 \; L/kgal \; x \; 29 \; kgal_{B-201 \; waste} \; x$

 $62 \text{ g/mole}_{NO3} \times MT/1e6g = 6.02 \text{ MT}$

K:

 $0.80 \, \mathrm{MT}$

Na:

3.41

Estimated component inventories from this engineering evaluation are compared with sampling- and HDW-estimated based inventories for selected components in Table D1-2. Observations regarding these inventories are noted by component in the following text. The complete HDW inventory is in Table A3-2.

Bismuth. This evaluation assumed Bi to precipitate 100 percent. Bismuth was used to determine the CF for this waste tank and for tanks 241-B-202 through B-204. This was accomplished by determining what CF would be necessary to bring the waste stream concentration, times the total waste volume, into agreement with the sampling data. This biases the data to match the sampling results for this one analyte. However, this CF is used for the other analytes, and the results agree with the sampling data (for example, manganese) indicating the CF is near the true CF for this tank. The Agnew HDW estimate is about 10 times lower than the sample. This appears to be caused by the assumption in the HDW that bismuth is partially soluble.

Table D1-2. Comparison of Selected Component Inventory Estimates.

Component	This Evaluation (MT)	Sampling-based (MT)	HDW Estimated (MT)
Bi	13 (used as basis)	13	1.34
K	0.796	0.799	0.943
La		2.08	3.49
NO ₃	6.02	6.78	8.72
Mn	2.94	2.64	0.0225
SO ₄		0.0479	0.019
Cr	·	0.459	0.0137
PO ₄		2.30	0.971
F		0.802	4.10
Na	3.41	5.25	11.00
H ₂ O %		60.7	57.1

Note:

MT = metric tons

Nitrate. The HDW estimated inventory is larger than the sampling-based inventory and both inventories are larger than the inventory estimated in this evaluation. The results of the flowsheet evaluation differs from the sampling analytical results by about 12 percent, which is good agreement. The HDW estimate is about 30 percent higher than the analytical results, which is reasonable agreement. The HDW estimated inventory is derived from the LANL-defined 224 waste stream, in which the nitrate concentration is about 30 percent higher than the Schneider flowsheet (Schneider 1951).

Sulfate. The HDW estimated inventory is smaller than the sampling-based inventory. Place's waste stream estimate (Kupfer et al. 1997) is about three times higher for sulfate than is Schneider's (1951). If the Place value is used in the HDW model, the HDW would probably more closely agree with the sample analytical data. Because almost everything else agrees with the sampling based inventory, further evaluation should be made between the sulfate concentrations of Place and Schneider.

Chromium. The HDW-estimated inventory is considerably lower than the sampling-based inventory. The data suggests that about 24 percent of the Cr precipitated; the HDW model assumes a much smaller percent.

Phosphate. The sampling-based phosphate value is over two times greater than the HDW value and is seven times greater than the flowsheet value. These values cannot be reconciled at this time.

Fluoride. The analytical sample evaluation is based on water soluble fluoride only. The sample value is about five times lower than the HDW value. No method is currently available to measure water insoluble fluoride in tank waste. Until a sample is analyzed by a methodology that measures total fluoride, these differences cannot be reconciled.

Sodium. The sodium values calculated assumed Na does not partition and slightly underpredicts the sample analysis values. The HDW value is approximately three times the value from this evaluation. The difference between the flowsheet values used here and the HDW value is approximately a factor of three also. It appears that if the HDW and flowsheet values were reconciled, they would agree.

Potassium. The HDW and sampling values for potassium agree fairly well.

Lanthanum. Lanthanum appears to partition between the phases in the tank. The partitioning factor for La was 38 percent indicating that more La could have been released to the cribs than remains in these tanks. Based on past expectations, this is not expected.

Manganese. This is an insoluble analyte, and the value from this evaluation is in good agreement with the sample analytical data. However, the HDW model treats this as highly soluble at the waste stream concentration and predicts about 75 times less manganese in the waste.

Total Hydroxide. Once the best basis inventories were determined, the hydroxide inventory was calculated by performing a charge balance with the valences of other analytes. In some cases this approach requires that other analyte (e.g., sodium or nitrate) inventories be adjusted to achieve the charge balance. During such adjustments the number of significant figures is not increased. This charge balance approach was consistent with that used by Agnew et al. (1996a).

Comments On Other Analytes

Strontium. The HDW model estimate for Sr is about 1,000 times higher than sampling results. The HDW model shows Sr in the 224 defined waste stream, apparently added for scavenging 90Sr. This is incorrect; scavenging should be shown in the ferrocyanide defined wastes.

Aluminum. The sampling-based data show almost one half ton of Al in the tank. The engineering analysis could not address aluminum quantitatively because it does not appear in the process flowsheet.

Plutonium. Although the amount of Pu was low, it was much higher than predicted by the HDW model. The process flowsheet did not contain plutonium values, so Pu could not be evaluated in the engineering analysis.

D1.5 CONCLUSIONS

The calculations based on the flowsheet information and factors determined from the bismuth analytical data from tank 241-B-201 have been compared to analytical data and the HDW model. These calculations compare well with the analytical data and, in some cases, with the HDW model. It appears that the flowsheet concentrations, the throughput factor, and the solubility assumptions applied in the HDW model account for the major differences.

The calculated CFs and partitioning factors for tank 241-B-201 provide confidence that the analytical data for the tanks are representative of the tank contents and could be used as a basis for component inventories. This is substantiated by the following:

- CFs for components in tank 241-B-201 that are expected to fully precipitate are consistent indicating the sample probably represents the 224 flowsheet basis for the waste.
- The partitioning factors indicate reasonable partitioning of components based on experience and knowledge of the typical chemical behavior of the components in alkaline media.

D2.0 BEST-BASIS INVENTORY ESTIMATE

Information about chemical, radiological, and/or physical properties is used to perform safety analyses, engineering evaluations, and risk assessment associated with waste management activities and to address regulatory issues. These activities include overseeing tank farm operations and identifying, monitoring, and resolving safety issues associated with these operations and with the tank wastes. Disposal activities include designing equipment, processes, and facilities for retrieving wastes, and processing them into a form suitable for long-term storage. Chemical and radiological inventory information are generally derived using three approaches: (1) component inventories are estimated using the results of sample analyses, (2) component inventories are predicted using the HDW model based on process knowledge and historical information, or (3) a tank-specific process estimate is made based on process flowsheets, reactor fuel data, essential material usage, and other operating data. The information derived from these different approaches is often inconsistent.

An effort is underway to provide waste inventory estimates that will serve as the standard characterization for the various waste management inventories (Kupfer et al. 1997). As part of

this effort, an evaluation of available chemical information for tank 241-B-201 was performed, including the following:

- Data from two 1991 core samples (this document).
- An inventory estimate generated by the HDW model (Agnew et al. 1996).

The calculations based on flowsheet information and factors determined from the bismuth analytical data from tank 241-B-201 have been compared to analytical data and the HDW model. These calculations compare well with the analytical data and, in some cases, with the HDW model. Given current resources, the best source of inventory data appears to be the analytical data which was obtained during the 1991 core sampling and analysis event. One analyte, for which the analytical data may not be the best source, is fluoride. Only the water soluble forms of fluoride are reported in the analytical data. Although the HDW model predicts more fluoride, water insoluble fluoride cannot be measured using current laboratory techniques. Both the analytical data and the HDW model values must be carefully considered for fluoride at the present time. Table D2-1 and D2-2 present the best-basis inventory estimates for the nonradioactive and radioactive waste components, respectively. The inventory values reported in Tables D4-1 and D4-2 are subject to change. Refer to the Tank Characterization Database (TCD) for the most current inventory values.

Best-basis tank inventory values are derived for 46 key radionuclides (as defined in Section 3.1 of Kupfer et al. 1997), all decayed to a common report date of January 1, 1994. Often, waste sample analyses have only reported 90Sr, 137Cs, 239/240Pu, and total uranium, or (total beta and total alpha) while other key radionuclides such as 60Co, 99Tc, 129I, 154Eu, 155Eu, and 241Am, etc., have been infrequently reported. For this reason it has been necessary to derive most of the 46 key radionuclides by computer models. These models estimate radionuclide activity in batches of reactor fuel, account for the split of radionuclides to various separations plant waste streams, and track their movement with tank waste transactions. (These computer models are described in Kupfer et al. 1997, Section 6.1 and in Watrous and Wootan 1997.) Model generated values for radionuclides in any of 177 tanks are reported in the Hanford Defined Waste Rev. 4 model results (Agnew et al. 1997a). The best-basis value for any one analyte may be either a model result or a sample or engineering assessment-based result if available. (No attempt has been made to ratio or normalize model results for all 46 radionuclides when values for measured radionuclides disagree with the model.) For a discussion of typical error between model derived values and sample derived values, see Kupfer et al. 1997, Section 6.1.10.

Best-basis tables for chemicals and only four radionuclides (90 Sr, 137 Cs, Pu and U) were being generated in 1996, using values derived from an earlier version (Rev. 3) of the Hanford Defined Waste model. When values for all 46 radionuclides became available in Rev 4 of the HDW model, they were merged with draft best-basis chemical inventory documents. Defined scope of work in FY 1997 did not permit Rev. 3 chemical values to be updated to Rev. 4 chemical values.

Table D2-1. Sampling-Based Best-Basis Inventory Estimates for Nonradioactive Components in Tank 241-B-201 (October 18, 1996).

	Total Inventory	Basis	20, 2220).
Analyte	(kg)	(S. M. or E) ²	Comment
Al	473	S	
Bi	13,000	S	
Ca	1,680	S	
C1	227	S	
CO ₃	0	M	
Cr	459	S	·
F	802 ³	S	Water soluble only
Fe	1,840	S	
Hg	0.0824	S	
K	799	S	
La	2,080	S	
Mn	2,640	S	
Na	5,250	S	
Ni	65.9	S	
NO ₂	121	S	
NO ₃	6,780	S	
OH ⁴	8,520	С	Charge balance calculation
Pb	187	S	
P as PO ₄	2,300	S	
Si	2,780	S	
S as SO ₄	47.9	S	
Sr	127	S	
TOC	325	S	
\mathbf{U}_{total}	21.5	S	
Zr	1.47	S	

Notes:

¹See Table B3-12.

²S = Sample-based, M = Hanford Defined Waste model, E = Engineering assessment-based ³Fluoride is based on water soluble portion only.

⁴C = Calculated by charge balance; includes oxides as hydroxides, not including CO₃, NO₂, NO₃, PO₄, SO₄, and SiO₃.

Table D4-2. Best-Basis Inventory Estimate for Radioactive Components in Tank 241-B-201, Decayed to January 1, 1994 (Effective July 2, 1996). (2 Sheets)

Tank 241-B-201	I, Decayed to Jan	uary 1, 1994 (Effe	ective July 2, 1996). (2 Sheets)
Analyte	Total	Basis	Comment
	Inventory	(S,M, or E)1	
-	(Ci)		
³H	5.63 E-04	M	·
¹⁴ C	0.0435	S	
⁵⁹ Ni	4.96 E-05	M	
⁶⁰ Co	5.60 E-05	M	
⁶³ Ni	0,00457	M ·	
⁷⁹ Se	3.68 E-05	M	
⁹⁰ Sr	287	S	
⁹⁰ Y	287	S	Based on 90Sr
^{93m} Nb	1.45 E-04	M	
⁹³ Zr	1.75 E-04	M	
⁹⁹ Tc	0.267	S	·
¹⁰⁶ Ru	4.20 E-11	M	
113mCd	4.89 E-04	M	
¹²⁵ Sb	6.46 E-05	M	
¹²⁶ Sn	5.55 E-05	M	
¹²⁹ [2.29 E-06	M	
¹³⁴ Cs	2.78 E-06	M	
^{137m} Ba	104	S	Based on ¹³⁷ Cs
¹³⁷ Cs	110	S	
¹⁵¹ Sm	0.139	M	V
¹⁵² Eu	1.82 E-04	M	
¹⁵⁴ Eu	0.602	S	
¹⁵⁵ Eu	0.0164	M	
²²⁶ Ra	8.22 E-09	M	
²²⁷ Ac	4.34 E-08	M	
²²⁸ Ra	5.29 E-13	M	
²²⁹ Th	1.02 E-10	М	
²³¹ Pa	1.00 E-07	М	
²³² Th	4.62 E-14	M	
²³² U	5.36 E-08	M	
²³³ U	2.45 E-09	M	
²³⁴ U	0,00267	М	
²³⁵ U	1.19 E-04	M	

Table D4-2. Best-Basis Inventory Estimate for Radioactive Components in Tank 241-B-201, Decayed to January 1, 1994 (Effective July 2, 1996). (2 Sheets)

Analyte	Total Inventory (Ci)	Basis (S,M, or E)	Comment
²³⁶ U	2.33 E-05	M	
²³⁷ Np	7.51 E-06	M	
²³⁸ Pu	3.21 E-04	M	
²³⁸ U	0.00271	M	
^{239/240} Pu	155	S	
²⁴¹ Am	4.26	S	
²⁴¹ Pu	0.0135	M	
²⁴² Cm	3.70 E-06	M	
²⁴² Pu	6.23 E-08	M	
²⁴³ Am	3.08 E-09	M	
²⁴³ Cm	7.98 E-08	M	
²⁴⁴ Cm	7.84 E-08	M	

¹S=Sample-based

M=Hanford Defined Waste model-based

E=Engineering assessment-based

D3.0 APPENDIX D REFERENCES

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